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Carbohydrate Research 324 (2000) 30–37

CARBOHYDRATE
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Lanthanide–saccharide chemistry: synthesis and characterisation of Ce(III)–saccharide complexes

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Received 6 July 1999; accepted 6 October 1999

Abstract

A series of nine Ce(III) complexes has been synthesised with seven different monosaccharides (D-glucose, D-fructose, D-galactose, D-mannose, L-sorbose, D-ribose and D-xylose) and two different disaccharides (D-maltose and L-lactose), and these have been characterised with various analytical, spectral, magnetic and electrochemical techniques. The NMR studies have highlighted some interesting features about the metal-ion-binding pattern of the saccharides. Some additional coordination has been proposed along with the chelating groups in the saccharide molecules, based on the shifts in ^{13}C NMR spectra. On the other hand, solution absorption studies and solid-state magnetic susceptibilities have indicated the contribution from the d-character to the spectral features to some extent.

Keywords: Ce^{3+}–saccharide complexes; Chelation by saccharide molecules; Metal-ion-induced ^{13}C NMR shifts; d-Character for the unpaired electron in Ce^{3+}

1. Introduction

During the past decade the coordination chemistry of lanthanides has made enormous progress, where the ligands employed range from simple acyclic to complex macrocyclic ones [1–4]. Besides the spectral as well as structural characterisation of certain complexes [5–7], their chemical, photochemical and biological reactivities have also been addressed in the literature [8–10]. As far as saccharides as ligands are concerned, the studies with the lanthanides are extended only up to interactions in solution. The solution studies in this context have primarily utilised NMR techniques [11,12]. In the case of lanthanides the isolated solid complexes of saccharides as ligands are still scant in the literature. While the transition metal saccharide chemistry has been very well studied in recent years, that of the lanthanides is still in its infancy. In view of the chemical, biological and industrial importance of saccharides, we have been motivated to address the saccharide chemistry of lanthanides also. Continuing our efforts in saccharide chemistry and biology of transition metal ions [13], this paper deals with a first attempt at the synthesis and characterisation of saccharide complexes of cerium(III).

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PII: S0008-6215(99)00277-3

2. Experimental

Methods and materials.—All solvents were distilled and dried prior to use by usual methods. All the saccharides and sodium metal were purchased from Aldrich Chemical Co. (USA) or Lancaster Synthesis Ltd. (UK) and used without further purification. Cerium acetate dihydrate was prepared by a literature method [14].

Absorption spectra were recorded using a Shimadzu UV-2101 spectrophotometer. FTIR spectra were recorded in KBr matrix on an Impact 400 Nicolet FTIR spectrometer. Elemental analyses were carried out on a Carlo–Erba elemental analyser. Cerium and sodium contents were determined using inductively coupled plasma–atomic emission spectroscopy (ICP–AES) Labtam Plasmalab 8440 analyser. CD experiments were performed on a Jasco J-600 spectropolarimeter. Thermal analysis was performed on a Shimadzu DT-30 thermal analyser. Cyclic voltammetry was carried out on a BAS-100 electrochemical analyser. EPR spectra were recorded on Bruker ESP-300 spectrometer. NMR studies were performed on a Bruker Advance DRX500 spectrometer.

Synthesis.—All complexes were prepared in an analogous procedure, and a typical procedure for synthesis is given below for one case.

Ce-D-*Glc* (**1**).—D-Glucose (0.540 g, 3 mmol) was suspended in 15 mL of dry MeOH and stirred for 30 min. Freshly cut sodium metal (0.138 g, 6 mmol) was added with stirring, and the stirring was continued for a further 4–6 h until a white suspension in MeOH was formed. Cerium acetate dihydrate (0.326 g, 1 mmol) was dissolved in 2 mL of distilled water and added dropwise to the sodium salt suspension. The resulting suspension was allowed to stir for a further 2 h to develop a light yellow–brown colour in the reaction mixture. The solid was then filtered, washed twice with a 1:10 water–MeOH mixture and thrice with dry acetone, and it was finally dried under vacuum for several hours to isolate a light-coloured solid in 45% yield.

All other monosaccharide complexes were prepared and isolated using the same procedure. Compounds **8** and **9** were also prepared adapting the same procedure, using 0.72 g (2 mmol) of disaccharide, 0.184 g (8 mmol) of sodium metal and 0.326 g (1 mmol) of $Ce(OAc)_3$ in 40 mL of dry MeOH.

All complexes reported in this paper were synthesised from Ce(III) starting material. However, when the syntheses were performed with Ce(IV) salt using ceric ammonium nitrate, a mixture of products was found to be formed and a pure product could not be isolated.

3. Results and discussion

General observations.—The complexes are all light in colour, almost off-white with a little brownish tinge, and are moderately air stable. But these complexes slowly capture moisture when kept exposed to air for 3–4 days, forming a brown pasty material. However, when the complexes are stored under dry conditions they do not change colour even over several weeks. The complexes are soluble in warm water, but insoluble in any common organic solvents. The elemental analyses and the molar conductance values agree well with the proposed composition of the complexes as reported in Table 1.

FTIR spectra.—The FTIR spectra of all the complexes (**1**–**9**) exhibited a broad-band pattern characteristic of metal-bound saccharide moieties [15]. Usual line broadening was observed in all the characteristic vibrations of the saccharides, revealing that there exists direct interaction of the metal ion with the saccharides, as observed earlier in the case of transition-metal–saccharide complexes. On the other hand, the spectra of simple adducts generally gave sharp signals [16]. The spectra of the disaccharide complexes (**8** and **9**) were also found to be similar to those of the monosaccharide complexes (**1**–**7**). The FTIR spectra of all the complexes are shown in Fig. 1, and the spectra of the corresponding ligands are shown in Fig. 2. A broad and intense band observed in the range 3350–3400 cm^{-1} is assignable to ν_{O-H} and indicates the breakage to some extent of the intermolecular hydrogen bonding, which is otherwise present in the solid of the free saccharides. However, the

Table 1
Composition, label, molar conductance and elemental analysis data of complexes **1**–**9**

Compound no.	Label	Composition	Molar conductance (ohm^{-1} M^{-1} cm^2)	Analysis (%)			
				C	H	Na	Ce
1	Ce-D-Glc	$C_{22}H_{46}CeNa_3O_{23}$	158	calcd 29.77	5.22	7.77	15.79
				obs 29.71	5.44	8.13	15.94
2	Ce-D-Fru	$C_{22}H_{42}CeNa_3O_{21}$	165	calcd 31.03	4.97	8.10	16.45
				obs 29.68	5.50	7.77	16.94
3	Ce-D-Gal	$C_{22}H_{46}CeNa_3O_{23}$	171	calcd 29.77	5.22	7.77	15.79
				obs 30.12	5.45	8.26	16.36
4	Ce-D-Man	$C_{22}H_{44}CeNa_3O_{22}$	168	calcd 30.38	5.10	7.93	16.11
				obs 29.86	5.63	7.12	16.61
5	Ce-D-Sor	$C_{22}H_{42}O_{21}Na_3Ce$	193	calcd 31.03	4.97	8.10	16.45
				obs 31.96	5.13	8.23	16.34
6	Ce-D-Rib	$C_{19}H_{37}CeNa_3O_{18.5}$	207	calcd 29.62	4.84	8.95	18.18
				obs 29.28	5.35	8.05	19.16
7	Ce-D-Xyl	$C_{19}H_{38}CeNa_3O_{19}$	187	calcd 29.27	4.91	8.85	17.97
				obs 30.00	5.34	7.92	17.03
8	Ce-D-Mal	$C_{15}H_{32}CeNaO_{16}$	50	calcd 28.53	5.11	3.64	22.19
				obs 28.14	5.53	3.71	23.34
9	Ce-D-Lac	$C_{16}H_{34}CeNaO_{16}$	86	calcd 29.77	5.31	3.56	21.71
				obs 30.04	5.51	3.59	22.08

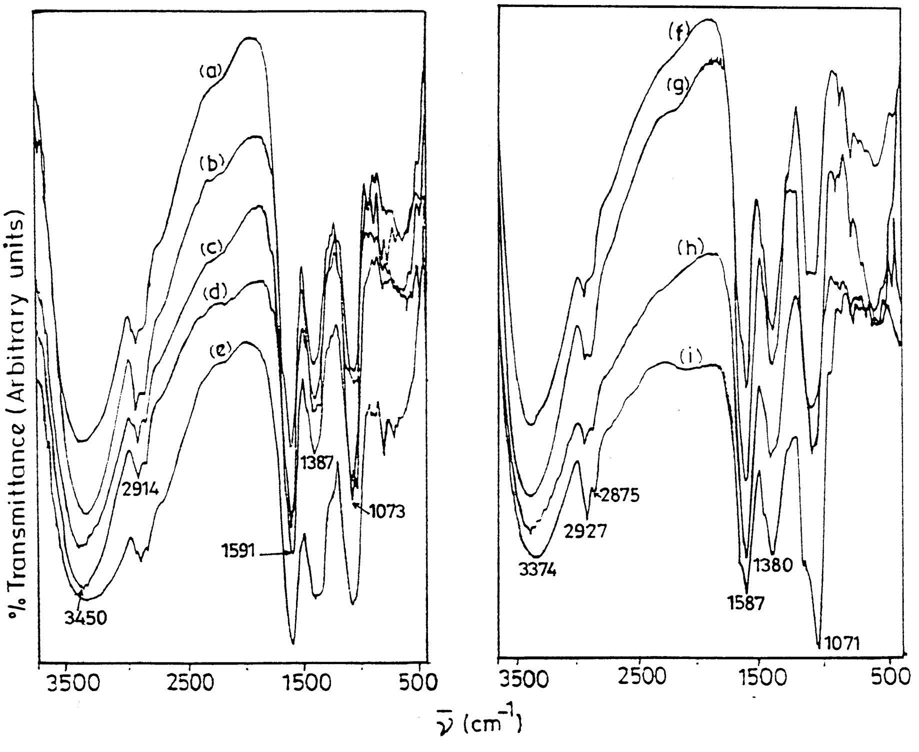

Fig. 1. FTIR spectra of the complexes: (a) Ce-D-Glc (**1**); (b) Ce-D-Fru (**2**); (c) Ce-D-Gal (**3**); (d) Ce-D-Man (**4**); (e) Ce-D-Sor (**5**); (f) Ce-D-Rib (**6**); (g) Ce-D-Xyl (**7**); (h) Ce-D-Mal (**8**); (i) Ce-D-Lac (**9**).

shape, position and the width of this band in the complexes are further indicative of the secondary interactions of saccharides through the free hydroxyl groups. The ν_{O-H} of H_2O also appears in this region and would overlap with this band. A band observed in the range 2850–2950 cm^{-1} is indicative of the C–H stretching vibrations in the complexes. Al-

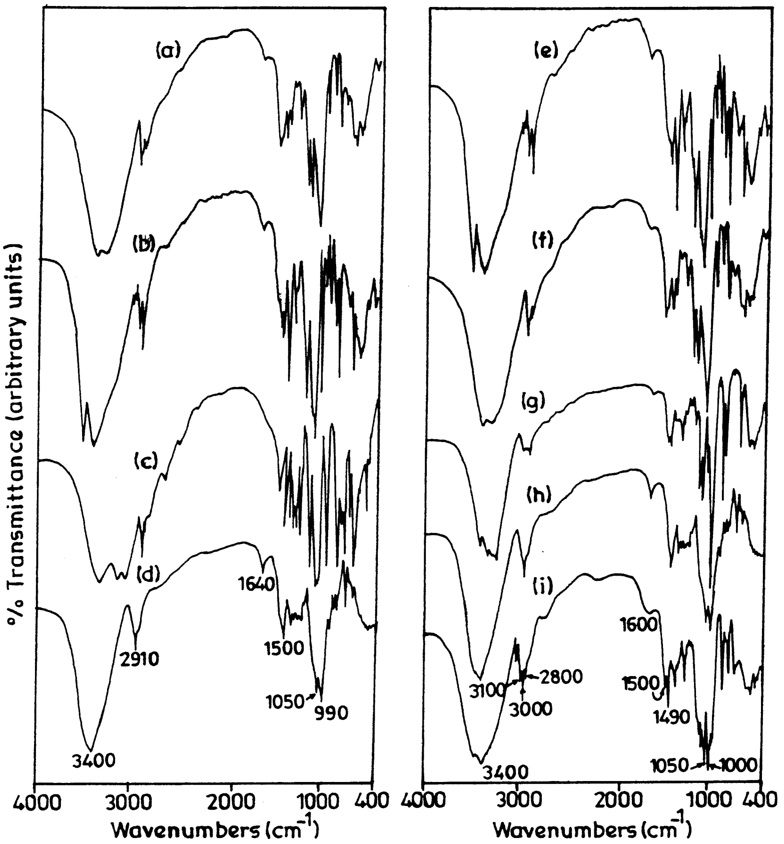

Fig. 2. FTIR spectra of the free saccharides: (a) D-Glc; (b) D-Fru; (c) D-Gal; (d) D-Man; (e) L-Sor; (f) D-Rib; (g) D-Xyl; (h) D-Mal; (i) D-Lac.

though one-to-one assignments were not possible, the bands that appeared in the regions 1600–1650, 1350–1450 and 1000–1100 cm^{-1} were assignable to the bending vibrations of H_2O, stretching vibration of CO, CC, and OCH, CCH, respectively. Thus, the FTIR studies have clearly demonstrated the binding of saccharide units to the metal ion and thereby exhibit the complex formation.

Thermal analysis.—Thermal analysis data for the complexes (**1**–**9**) with appropriate assignments of the fragments are shown in Table 3. The data show the presence of one or two solvent molecules of acetone and/or MeOH, along with a varying number of water molecules in the range 1–3. A 60–70% weight loss was observed during the total temperature scan range (25–600 °C), indicating the loss of all the solvent molecules and the ligating saccharide moieties, leaving the oxides of cerium behind. Similar thermal degradation patterns were observed in case of the saccharide complexes of Cr(III), Mn(II), Fe(III), and Mo(VI) [17].

Solution absorption and solid-state diffused reflectance spectra.—The aqueous solution absorption spectra were recorded in the range 190–800 nm, and the corresponding data are reported in Table 2. The solution absorption bands are observed mainly at three positions, ~230, ~330 and ~360 nm, and were found to be broad. The spectra of all the complexes are shown in Fig. 3. These broad absorption bands can be attributed to the saccharide–oxo → Ce^{3+} charge-transfer transition. How-

Table 2
Aqueous solution absorption data for **1**–**9**

Compound no.	λ (ε) (nm) (LM^{-1} cm^{-1})
1	257(1940), 329(1290), 367(950)
2	264(2860), 366(1100)
3	274(4250), 332(3220), 368(2140)
4	272(3320), 330(2470), 366(2000)
5	269(4850), 366(2340)
6	271(5490), 333(3310), 367(2340)
7	271(3910), 329(2870), 364(2310)
8	274(3220), 330(2530)
9	273(9280), 324(7760)

Table 3
Thermal analysis data for complexes **1**–**9**

Compound no.	Temperature	% Weight loss	Possible fragments lost
1	40	6.0	CH_3COCH_3
	80	6.5	CH_3OH+H_2O
	130	4.5	$2H_2O$
	215	10.5	CO_2+2H_2O
	235	24.5	$3CO+3H_2O$
	330	6.0	CO
	425	5.0	CO
2	85	8.0	$CH_3COCH_3+H_2O$
	115	4.0	CH_3OH
	195	11.0	CO_2+2H_2O
	230	6.5	$CO+H_2O$
	250	22.0	$3(CO+H_2O)$
	445	12.5	$CO+2H_2O$
3	70	8.0	$CH_3COCH_3+H_2O$
	135	8.0	CH_3OH+2H_2O
	220	16.0	CO_2+2H_2O
	325	21.0	$3CO_2$
	270	9.0	$CO+H_2O$
	435	6.5	CO
4	70	6.5	CH_3COCH_3
	150	8.5	CH_3OH+2H_2O
	240	15.5	$2CO_2+1.5H_2O$
	260	13.0	CO_2+2H_2O
	335	13.0	$2CO+H_2O$
	430	8.5	$CO+H_2O$
5	70	6.5	CH_3COCH_3
	105	2.5	H_2O
	200	8.5	CH_3OH+2H_2O
	240	8.0	CO_2+H_2O
	260	8.5	2CO
	285	15.5	$2(CO+H_2O)$
	445	9.0	$CO+H_2O$
6	60	8.5	CH_3COCH_3 $+0.5H_2O$
	120	6.5	CH_3OH+H_2O
	190	6.5	CO_2
	235	18.5	$2CO+3H_2O$
	300	11.5	2CO
	440	6.0	CO
7	60	7.0	CH_3COCH_3
	125	8.0	$CH_3OH+1.5H_2O$
	195	8.0	$CO_2+0.5H_2O$
	225	22.5	$3(CO+H_2O)$
	315	8.5	$CO+H_2O$
	440	5.5	CO
8	80	9	CH_3COCH_3
	140	6.5	$2H_2O$
	215	13.5	$2CO+H_2O$
	230	4	H_2O
	255	25.5	4CO
	290	5.5	H_2O
	440	5.5	0.5CO
9	50	8	CH_3COCH_3
	90	5	CH_3OH
	175	10	CO_2+H_2O
	235	24	$4CO+0.6H_2O$
	265	9	$2H_2O$
	310	7.5	CO
	415	3.5	0.5CO

ever, the electronic transitions in lanthanides are expected to show sharp signals, because the perturbation due to external field is minimum in case of the deep-seated f orbitals. But it is also true that if the f electron is excited to any of the higher orbitals $\{(n+2)$s, $(n+2)$p or $(n+1)$d$\}$, the spectrum is expected to broaden. Also, broadening of the spectrum is possible in case of charge-transfer transitions in lanthanides [18]. These facts fully support our observation in case of Ce^{3+} saccharide complexes. In case of Ce(III), it is possible to populate the 5d level; thus, the absorption band could result in broadening. The diffused reflectance spectra of the solid complexes showed broad bands in the same positions corresponding to those observed in solution. Thus, these studies indicated the retainment of the solid-state structure upon dissolution.

Solid-state magnetic and EPR studies.—Room temperature (rt) magnetic susceptibility measurement of the powdered complexes (**1**–**9**) showed the μ_{eff} values in the range 2.05–2.62 μ_B. The calculated magnetic moment for Ce^{3+} ion using the appropriate μ_J expression is 2.49 μ_B[1]. Although the values in the present case are higher than the spin-only magnetic moment of a single electron (1.732 μ_B), some of the values are found (**1**, **3**, **4**, **6**, **8** and **9**) to be less than the calculated one. This is possible in the case of Ce(III) at rt because the energy separation between 4f and 5d is rather small. When the electron is transferred to the 5d orbital, the involvement of d quenches the contribution from spin–orbit coupling to some extent.

The X-band EPR spectra measured for the powdered complexes (**1**–**9**), both at rt as well as at liquid-nitrogen temperatures, exhibited broad signals characteristic of lanthanide complexes.

Circular dichroism.—The circular dichroism spectra of all the complexes (**1**–**9**) in aqueous solution exhibited bands in the wavelength range 215–400 nm. The monosaccharide complexes (**1**–**7**) showed a positive Cotton effect in the vicinity of the 220 nm absorption, which indicates that the metal ion is at the

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[1] $\mu_J = g[J(J+1)]^{1/2}$ μ_B where J is for the ground-state level, which in case of cerium(III) is the lowest $L+S$ value and $g = 1 + \{J[J+1] + S[S+1] - L[L+1]/2J[J+1]\}^{1/2}$.

centre of the dissymmetry of the saccharide moieties. Although the Cotton effect is not very prominent in the case of the disaccharide complexes (**8** and **9**), the sign of the CD curve was found to be similar to that of the monosaccharide complexes. The spectral results indicate similarities in the configuration around the metal centre in these complexes.

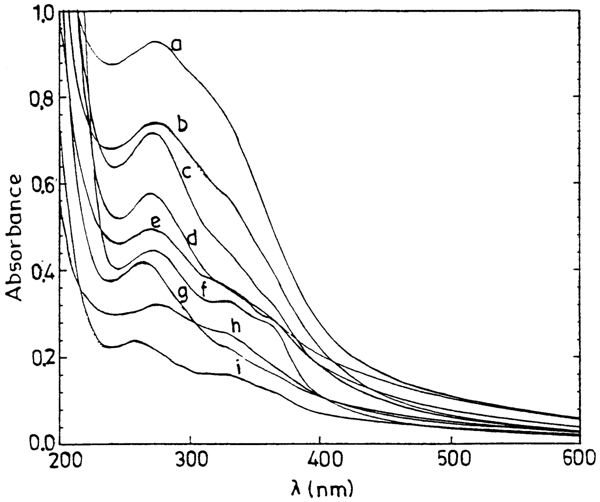

Fig. 3. Aqueous solution absorption spectra of the complexes: (a) Ce-D-Mal (**8**); (b) Ce-D-Gal (**3**); (c) Ce-D-Rib (**6**), (d) Ce-D-Sor (**5**); (e) Ce-D-Xyl (**7**); (f) Ce-D-Man (**4**); (g) Ce-D-Fru (**2**); (h) Ce-D-Lac (**9**); (i) Ce-D-Glu (**1**).

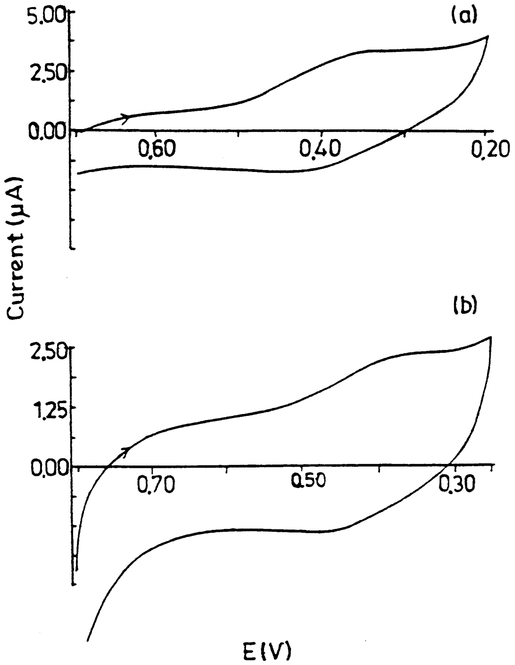

Fig. 4. Cyclic voltammograms of (a) Ce-D-Man (**4**) and (b) Ce-D-Lac (**9**), using Pt working and Ag | AgCl reference electrode in 0.1 M KCl as supporting electrolyte at a scan speed of 100 mV.

Cyclic voltammetry.—The cyclic voltammograms of all the complexes were measured in 0.1 M aq KCl using Ag | AgCl as reference and Pt as working electrodes. Some selected voltammograms (**4** and **9**) are shown in the Fig. 4. All complexes have shown a quasireversible couple for the Ce^{3+}/Ce^{4+}, judged based on the peak separation and the current height. These are observed at (+400/+476), (+490/+550), (+550/+490), (+360/+440), (+360/+480), (+380/+470), (+380/+490), (+375/+450) and (+390/+450) mV, respectively, for complexes **1**–**9**, where the first value in the pair indicates the cathodic peak potential (E_p^c, mV) and the second refers to the anodic peak potential (E_p^a, mV). An irreversible electron transfer is also observed on the cathodic side in the range +100 to +200 mV, which could probably be assigned to the Ce^{3+}/Ce^{2+} redox process.

NMR studies.—The ^{13}C NMR spectrum of each complex was compared with that of the corresponding free saccharide molecule. The complexation shifts ($\Delta\delta$ ppm $= \delta_{\text{complex}} - \delta_{\text{ligand}}$) are given in Table 4. It was found that the pyranose form of the saccharide (α or β) is predominant in all the complexes. The preferential interaction of one oxo group of the saccharide over the other has been identified as earlier from the amount of shift suffered by the corresponding carbon signals, as reported by us earlier in case of molybdenum complexes [17(d)]. It has been shown in the literature that when the monosaccharide has the arabinopyranose conformation, the interaction with the metal ion is site specific, involving the C-3 and C-4 hydroxyls. Also, it is worth noting that the affinity of lectins towards saccharides is sensitive to the orientations of the OH groups at C-3 and C-4 [19]. Apart from the usual binding of saccharide molecules through the deprotonated hydroxyl groups, some additional metal–ligand interactions are predicted from the undeprotonated hydroxyls of the same saccharide molecule, based on the $\Delta\delta$ values. This is supported by the fact that cerium can very well extend its coordination sphere beyond six. While large $\Delta\delta$ values were assigned to saccharide–O$^-$ bound to the metal ion, the smaller $\Delta\delta$ values are assigned to saccharide–OH binding, indi-

Table 4
$\Delta\delta$ (ppm) values (^{13}C) for complexes **1**–**9**

Compound	C-1		C-2		C-3		C-4		C-5		C-6	
1	x [b]		1.67		3.17		4.53		4.32		5.19	
2	1.58		3.44		6.88		5.79		11.94		0.617	
3	1.71		0.96		3.63		6.38		1.43		2.97	
4	x		1.83		5.90		5.53		3.92		2.96	
5	1.58		0.50		3.62		4.69		4.04		0.99	
6	x		2.55		1.72		2.47		1.65			
7	x		1.22		1.78		2.69		2.35			
	C1′ [a]	C1	C2′	C2	C3′	C3	C4′	C4	C5′	C5	C6′	C6
8	3.89	3.88	0.80	1.27	4.33	3.95	6.58	x	0.38	0.21	0.25	0.11
9	3.93	7.18	2.86	3.62	5.98	3.62	6.78	x	x	x	1.00	1.12

[a] C′ indicates the carbon atoms from the non-reducing part of the disaccharides.

[b] 'x' means the value could not be obtained.

cating the difference in the binding strength of these two types. Based on the complexation shifts given in the Table, the following is evident: (i) aldohexoses (**1**, **3** and **4**) chelate through O-3 and O-4 and give the additional coordination through OH-6; (ii) ketohexoses (**2** and **5**) chelate through O-4 and O-5 as favourable ones, with an additional coordination through OH-3; (iii) aldopentoses (**6** and **7**) interact only through O-2, O-3 and O-4, among which O-2 and O-3 are predicted to be chelated and the other is weakly interacting and (iv) in the case of the disaccharides a tridentate chelation is predicted along with one or two additional interactions extended through the OH groups. Therefore maltose (**8**) can act as an O-3′–O-4′–O-3 chelate, whereas lactose (**9**) can act as an O-3′–O-4′–O-2 chelate to the metal ion. Besides these chelations, weak interactions may come from OH-2′ and OH-2 in the case of **8** and OH-6′ and OH-1 in the case of **9**. Thus, the saccharide moieties have shown not only the binding of O^-, but also the OH binding to the metal centre.

The ^{1}H NMR spectra were found to be broad and complex, and hence individual resonances could not be resolved. However, the total range of the skeletal protons of the saccharide molecule was found to be shifted downfield upon coordination in the complexes.

Nature of the products.—While the FTIR and absorption spectra have demonstrated the direct binding of the saccharide moieties with the Ce(III) ion, the NMR studies have delineated the binding of specific oxo ($-O^-$) and hydroxy (–OH) groups to the metal centre in all the complexes (**1**–**9**). This approach of assignment based on NMR spectroscopy has taken the advantage of magnitude of shift ($\Delta\delta$) and the chelating nature of the adjacent hydroxyl groups present on the saccharide moiety. On the other hand, the thermal degradation experiments have elicited the fragmentation pattern and also indicated the total loss of organic moiety present in the complexes. The CD spectra have demonstrated the dissymmetry present around the metal ion in the field of the saccharide moieties. If the single electron that was present in the 4f orbital was to be shifted to that of the 5d, one would expect concomitant changes in the absorption spectra and also in the magnetic susceptibility measurements. Although the μ_{total} was found to be certainly higher than the spin-only value, several of the complexes (**1**, **3**, **4**, **6**, **8** and **9**) exhibited a μ_{total} that is lower than the expected value of 2.49 μ_B, which includes the total contribution of spin-orbit coupling. If the d-character were to be considered, a lowering of spin–orbit coupling is expected. The molar conductance values for monosaccharide complexes (**1**–**7**) are found in the range 160–200 ohm^{-1} M^{-1} cm^2, whereas those of the disaccharide complexes (**8** and **9**) are in the range 50–90 ohm^{-1} M^{-1} cm^2. The conductance data suggest a 3:1 electrolyte behaviour [17(a)] for **1**–**7** and a 1:1 electrolyte behaviour for **8** and **9**. Thus, the data support the presence of a trinegative complex anion of the formula $[Ce(sacch)_3]^{3-}$ for monosaccharide complexes and a monoanionic core of the formula $[Ce(disacch)(OH)(H_2O)_2]^{1-}$ for disac-

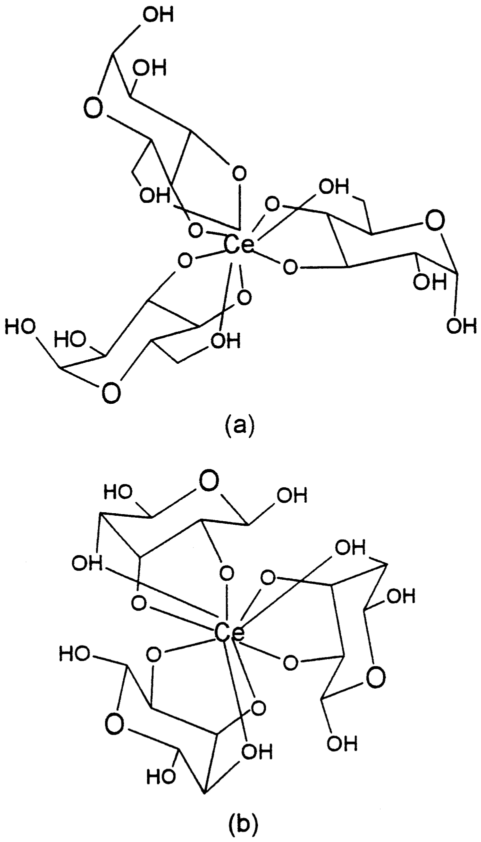

Fig. 5. Proposed structures of (a) Ce-D-Glc (**1**) and (b) Ce-D-Rib (**7**).

charide complexes. The elemental analysis data agree well with our proposed composition of the complexes. A combination of the analytical results with those of spectral, electrochemical and magnetic studies has resulted in the proposition of the complexes as follows: (i) $Na_3[Ce(sacch)_3]\cdot CH_3OH\cdot CH_3COCH_3\cdot nH_2O$ for the monosaccharides, where $n = 1$ for **2** and **5**; $n = 1.5$ for **6**; $n = 2$ for **4** and **7** and $n = 3$ for **1** and **3**; (ii) $Na[Ce(Mal)(OH)(H_2O)_2]\cdot CH_3COCH_3\cdot H_2O$ for **8** and (iii) $Na[Ce(Lac)(OH)(H_2O)_2]\cdot CH_3COCH_3CH_3OH$ for **9**. Representative structures of the complexes (**1** and **7**) shown in Fig. 5 are basically derived from the NMR data.

Acknowledgements

C.P.R. acknowledges the Department of Science and Technology, New Delhi, the Department of Atomic Energy, Mumbai, and the Council of Scientific and Industrial Research, New Delhi, for financial support. The UV-2101 PC was purchased from DST funds. We thank Professor S. Mitra, TIFR, Mumbai, for the CD and Dr M.D. Shastry and Dr R.M. Kadam, BARC, Mumbai, for EPR measurements. We thank Mr R. Kauppinen, Jyväskylä University, for some experimental help.

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